

54: Title of invention - Silicone gel composition and cosmetic product containing the said composition.

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#### Specification

##### 1. Title of invention

A silicone gel composition and a cosmetic product containing the said silicone gel composition.

##### 2. claims

(1) A silicone gel composition consisting of

(a) organopolysiloxane polymer prepared by the addition reaction between

(i) organohydrogenpolysiloxane having at least two hydrogen atoms binding to silicone atom in one molecule, and

(ii) organopolysiloxane containing at least two aliphatic unsaturated group binding to silicone atom in one molecule,

and

(b) low viscosity silicone oil.

(2) A cosmetic product containing the silicone gel composition described in the claim (1).

##### 3. Detailed explanation of the invention

( Industrial application )

The present invention refers to a silicone gel composition consisting of special organopolysiloxane polymer and low viscosity silicone oil, and a cosmetic product containing the said silicone gel composition. In other words, the purpose of the present invention is to provide a soft and stable silicone gel composition which is useful as a cosmetic ingredient and a safe cosmetic product exhibiting refreshing and smooth use feeling, excellent usability and fine storage stability which can

be prepared by adding the said silicone gel composition.

( Conventional technology )

Silicone oils have been used widely in various products because the silicone oils have excellent characteristics. Especially, silicone oils were used in cosmetic products as excellent oil ingredients. In other words, silicone oil can provide smooth and refreshing feeling and fine extendability on the skin without generating sticky feeling, and has a lubricating and water-repelling activity, and at the same time, is tasteless, odorless and safe on the skin. Accordingly, when the said silicone oil is added to a cosmetic product, a fine use feeling and protective action on skin and hair and a durability of activity can be improved significantly.

Silicone oils used in the conventional cosmetic products are chain form of dimethylpolysiloxane having various molecular weights and viscosity, cyclic octamethylcyclotetra siloxane, decamethyl cyclopenta siloxane or methylphenylpolysiloxane, methylhydrogen polysiloxane, and so on. In addition to the said compounds, various kinds of polymers, copolymers, **denatured products**, and so on are on the market today.

Various kinds of silicone oils are usually combined to obtain the best effect according to the purpose of use. For example, when a low viscosity dimethylpolysiloxane is added to a cosmetic product, a cosmetic composition showing less stickiness and fine refreshing feeling can be obtained. On the other hand, a high viscosity compound can be used in a product requiring a water-repelling effect. Since the chain or cyclic form of volatile silicone is evaporated after coating, the compound can be used in a cosmetic product requiring a refresh feeling after applying on the skin. Dimethyl hydrogen polysiloxane is added to a make-up cosmetic composition to improve the water-repelling activity of the powder make-up preparation.

( Problems solved by the invention )

As described above, although silicone oils are very important materials for cosmetic compositions as an oil agent, there are many weak points explained in the following.

In other words, the relative solubility of silicone oil in other ingredients of cosmetic products is considerably poor. In this case, stable and uniform product containing silicone oil as the base can not be prepared easily. Consequently, in case of adding silicone oil to the cosmetic composition, an emulsion form may be required. However, the storage stability of the composition is considerably poor. Furthermore, when a large amount of silicone oil is added to improve the special characteristics of the composition, a separation of silicone occurs with time. The said problem was especially visible when low viscosity or volatile silicone oil is added to improve the refreshing feeling of make-up cosmetic products. On the other hand, when a high

viscosity silicone oil is used, stickiness is induced although the water-repelling activity can be improved. Thus, a stable product containing a large amount of silicone oil has been requested.

As the conventional silicone oils have no yield value as the fluid characteristics, it is very difficult to achieve a stable dispersion of substances showing different specific gravity such as pigment, etc. when the said silicone oil was used as the major ingredient of the cosmetic product. As a result, the conventional product employed a high viscosity and large molecular weight silicone to improve the dispersibility. However, the sedimentation of ingredients and stickiness were induced when the said high viscosity and large molecular silicone oil was employed. On the other hand, when waxes are combined with the said silicone oil, the relative solubility is deteriorated and the precipitation of wax occurs. In other words, a stable product expressing a strong characteristics of silicone oil cannot be obtained.

( Method of solving the problems )

Under the said circumstance, the present inventors have investigated thoroughly silicone gel compositions to solve the problems described above. As a result, it was found that the purpose of the present invention could be accomplished by a combination of organopolysiloxane polymer having swelling three dimensional crosslinking structure which was insoluble in silicone oil, and low viscosity silicone oil. In this case, the silicone gel composition showing softness and fine storage stability was obtained. Furthermore, when the said silicone gel composition was added to a cosmetic product, the cosmetic composition demonstrated a smooth and refreshing use feeling, excellent usability and fine storage stability. Thus, the present invention was accomplished by utilizing the said knowledge.

In other words, the present invention relates to a silicone gel composition consisting of the following ingredients (a) and (b) and a cosmetic product containing the said silicone gel composition;

- (a) organopolysiloxane polymer prepared by the addition reaction between
  - (i) organohydrogenpolysiloxane having at least two hydrogen atoms binding to silicone atom in one molecule, and
  - (ii) organopolysiloxane containing at least two aliphatic unsaturated group binding to silicone atom in one molecule,

and

- (b) low viscosity silicone oil.

The present invention is explained in the following.

The silicone gel composition described in the present invention is insoluble in silicone oil and consists of sufficiently swelling organopolysiloxane polymer and low viscosity silicone oil. In other words, the low viscosity silicone oil is included in the organopolysiloxane polymer structure.

The said organopolysiloxane polymer is prepared by the polymerization ( addition polymerization ) of organohydrogen polysiloxane and organopolysiloxane containing aliphatic unsaturated group, and has a three dimensional crosslinkage structure.

Organohydrogen polysiloxane employed in the present invention consists of  $\text{HSiO}_{1-5}$  units,  $\text{RSiO}_{1-5}$  units,  $\text{RHSiO}$  unit,  $\text{R}_2\text{SiO}$  unit,  $\text{R}_2\text{HSiO}_{0-5}$  unit,  $\text{R}_3\text{SiO}_{0-5}$  unit, etc. The molecular structure of the compound may be linear, branched or cyclic and contains at least two hydrogen atoms binding to silicone atom in one molecule. It is preferable that organohydrogen polysiloxane used in the present invention is linear form in order to control the organopolysiloxane polymer polymerization reaction. It is claimed in general that hydrogen atom (  $\text{SiH}$  bond ) binding to silicone atom in organohydrogen polysiloxane is included in the molecular chain. However, it may be at the terminal of the molecular chain. In case of linear or branched chain structure, the amount of the said  $\text{SiH}$  bond is usually 1 - 20 mol %. In case of cyclic structure, it is preferably 1 - 50 mol %. The concentration of organic groups other than  $\text{SiH}$  bonds may be at least 50 mol % of methyl group, preferably.

Organopolysiloxane containing aliphatic unsaturated group used in the present invention is the compound having at least 2 aliphatic unsaturated groups binding to silicone atom in one molecule. The said organopolysiloxane may be vinyl group and aryl group, and it is usually organovinyl polysiloxane containing vinyl group. Organopolysiloxane consists of  $(\text{CH}_2-\text{CH})\text{SiO}_{1-5}$  unit,  $\text{RSiO}_{1-5}$  unit,  $\text{R}(\text{CH}-\text{CH}_2)\text{SiO}$  unit,  $\text{R}_2\text{SiO}$  unit,  $\text{R}_2(\text{CH}-\text{CH}_2)\text{SiO}_{0-5}$  unit,  $\text{R}_2\text{SiO}_{0-5}$  unit, etc. The molecular structure may be linear, branched or cyclic and contains at least two aliphatic unsaturated groups such as vinyl group, etc. binding to silicone atom in one molecule. Organopolysiloxane containing aliphatic unsaturated group employed in the present invention is preferably linear form in order to control the organopolysiloxane polymer polymerization reaction. Furthermore, although it is claimed in general that the said organovinyl polysiloxane is a linear type compound in which both terminals of molecular chain are sealed with dimethylvinyl silyl group, the said vinyl group may be included in the chain structure. In case that the molecular structure is linear or branched, the concentration of vinyl group is 1 - 20 mol %. In case of branched type, it is preferably 1 - 50 mol %. At least 50 % of the organic group other than the vinyl group is preferably methyl group. Organohydrogen polysiloxane and organopolysiloxane containing aliphatic unsaturated group such as organovinyl polysiloxane contain at least 2 hydrogen atoms or vinyl groups binding to silicone atoms which are the reactive group in the molecule. In other words, the said structure is essential to form a three dimensional structure of the addition polymer. When the concentration of reactive groups in organopolysiloxane exceeds 20 mol % for linear or branched compounds, or 50 mol % for cyclic

compounds, the polymer becomes hard and the purpose of the present invention can not be accomplished. In other words, a low viscosity silicone oil can not be oriented into the three dimensional structure of the compound. In this case, the separation of silicone oil occurs and the stability of the composition is deteriorated. In contrast, when the concentration of the said reactive groups is less than 1 mol %, the structural viscosity becomes poor. Accordingly, in order to obtain a fine silicone gel composition showing softness and excellent storage stability, it may be preferable that the concentration of the reactive groups is 1 - 20 mol for linear or branched structure compounds and 1 - 50 mol % for cyclic structure compounds.

The said organic groups R in organohydrogen polysiloxane are alkyl groups such as methyl group, ethyl group, propyl group, butyl group, etc.; aryl groups such as phenyl group, tolyl group, etc.; cyclohexyl group; or non-substitution or substituted monovalent hydrocarbon groups excluding aliphatic unsaturated groups such as vinyl group, etc. selected from groups in which a part or a total hydrogens binding to carbon atoms of the said groups are substituted with halogen atoms, cyano group, etc.

The typical examples of the said compounds are methyl hydrogen polysiloxane consisting of the following unit;  $(CH_3)_2SiO \cdot \{ (CH_3)_2SiO \}_n$ .

$(CH_3)_2SiO \cdot Si(CH_3)_2 \cdot (n=10 \sim 500, n=2 \sim 50)$  and the compounds are preferable materials for the present invention.

The said organic group R of organo vinyl polysiloxane which is organo polysiloxane containing aliphatic unsaturated group are same as R of organo hydrogen polysiloxane. The typical examples of the said

compounds are methyl vinyl polysiloxane consisting of the following units;  $(CH_2=CH)(CH_3)_2SiO \cdot \{ (CH_3)_2SiO \}_n \cdot Si(CH_3)_2(CH=CH_2) \cdot (n=10 \sim 100)$  or  $(CH_3)_2SiO \cdot \{ (CH_3)_2SiO \}_n \cdot \{ (CH=CH_2)CH_2SiO \}_m \cdot Si(CH_3)_2 \cdot (n=10 \sim 500, m=2 \sim 50)$

and these can be used singly or a mixture of more than two compounds.

The addition reaction of organohydrogen polysiloxane and organo polysiloxane containing aliphatic unsaturated group can be made by the conventional method. For example, organo hydrogen polysiloxane and organovinyl polysiloxane are mixed wherein molar ratios of hydrogen group binding to silicone atom and vinyl group as the reactive group is 1/3 - 3/1, and an addition polymerization catalyst such as platinum, vanadium, etc. is added to the reaction system, and the reaction mixture is heated. In this case, the target compound

organopolysiloxane polymer which is insoluble in silicone oil can be prepared easily. The preferable addition polymerization catalyst may be chloroplatinic acid as described in Patent Journal Sho 33-9969.

On the other hand, low viscosity silicone oils described in the present invention are not particularly specified and any silicone oils showing less than 50 cs in the viscosity can be employed in the present invention. When a large amount of high viscosity silicone oil is used

in the composition, the greasy feeling is promoted and the use feeling of the composition is deteriorated. The low viscosity silicone oils are dimethyl polysiloxane of low polymerization degree, methyl phenyl polysiloxane, cyclic octamethyl cyclotetra siloxane, decamethyl cyclopentasiloxane, and so on. These compounds can be used singly or as a combination of more than two compounds.

The silicone gel composition described in the present invention is easily prepared by mixing organopolysiloxane polymer prepared by the method described above and a low viscosity silicone oil and the mixture is kneaded and allowed to swell. In this case, the composition ratio of organopolysiloxane polymer to low viscosity silicone oil is 5 : 95 - 30 : 70, weight %, preferably 10 : 90 - 25 : 75 weight %. When the concentration of organo polysiloxane polymer is small, the low viscosity silicone oil becomes excess. As a result, a fine gel structure can not be retained. In contrast, when the concentration of organo polysiloxane polymer is large, a soft gel composition can not be obtained.

The silicone gel composition prepared by the method described in the present invention exhibits an excellent retainability of low viscosity silicone and a fine storage stability, and at the same time, demonstrates a soft and refreshing use feeling and usability. When the said silicone gel composition is added to a cosmetic product, various characteristics of silicone oil can be generated.

The cosmetic products are basic cosmetic compositions such as cream, lotion for facial and skin care; hair care compositions such as hair conditioner, shampoo, rinse, etc.; make-up cosmetic compositions such as foundation, facial powder, cheek rouge, eyeshadow, lipstick, nail-care, etc. and so on. The cosmetic products are not particularly specified as long as the silicone gel composition can be added. The silicone gel composition may be added as an emulsion form or may be mixed with other ingredients. In this case, the concentration of the silicone gel composition in the cosmetic product is 5 - 100 weight %, and is properly determined according to the purpose of use.

The cosmetic product described in the present invention consists naturally of the said silicone gel composition and the ingredients used in the conventional cosmetic products. The basic ingredients of the conventional cosmetic products are oils and fats, waxes, hydrocarbons, fatty acids, higher alcohols, esters, metal soaps, silicone oils and other oil ingredients; powder ingredients such as white pigment, coloring pigment, constitutional pigment, etc.; surfactants; polyhydric alcohols, polymer compounds, water, preservatives, alkali agent, ultraviolet absorbing agent, tar pigment, skin care ingredients, and so on. These ingredients are selected properly according to the purpose of use.

( Practical examples )

The present invention is explained in detail in the following practical

examples. However, the scope of the present invention is not limited to the following practical examples.

#### Practical example 1

A 1750 g of trimethyl silyl terminal sealed dimethyl methyl hydrogen polysiloxane ( average molecular weight : 2340; Si-H 4.5 mol % ) and 710 g of dimethyl vinyl silyl terminal sealed dimethyl polysiloxane ( average molecular weight : 930; vinyl group 7.7 mol % ) were placed in a mixer ( approximately 5 liters in the capacity ) and were mixed by stirring.

A 7.5 g of 2 % isopropanol solution of chloroplatinic acid was added to the said mixture, and the temperature was raised at 70 - 80° C and the reaction was carried out for 2 hours with a constant stirring. After reducing the pressure to 5 - 10 mmHg, a stripping was continued for 30 min. As a result, white soft powder organopolysiloxane gel polymer was obtained.

A 2 weight parts of organopolysiloxane polymer and 8 weight parts of dimethyl polysiloxane ( viscosity : 5 cs ) were dispersed and mixed, and were kneaded thoroughly by a Miki roller. After swelling, a silicone gel composition was obtained.

#### Practical example 2

A 880 g of dimethylhydrogen silyl terminal sealed dimethylpoly siloxane ( average molecular weight : 2720; Si-H 2.6 mol % ) and 1620 g of trimethyl silyl terminal sealed dimethyl methyl vinyl polysiloxane ( average molecular weight : 5000; vinyl group 1.5 mol % ) were mixed and 0.5 g of 2 % isopropanol solution of chloroplatinic acid was added, and the reaction was carried out in the same manner as described in the practical example 1. Thus, a silicone gel composition was obtained.

#### Practical example 3

A 55 g of methyl hydroxy cyclotetrasiloxane ( average molecular weight : 232, Si-H 50 mol % ) and 2200 g of dimethylvinylsilyl terminal sealed dimethyl polysiloxane ( average molecular weight : 4400; vinyl group 1.3 mol % ) were mixed and 0.5 g of 2 % isopropanol solution of chloroplatinic acid and the reaction was carried out in the same manner as described in the practical example 1. Thus, a silicone gel composition was prepared.

#### Comparative example 1

A 1100 g of trimethyl silyl terminal sealed dimethyl methyl hydrogen polysiloxane ( molecular weight : 2200; Si-H 24 mol % ) and 1400 g of trimethylsilyl terminal sealed dimethylmethyl vinyl polysiloxane ( average molecular weight : 2780; vinyl group 21 mol % ) were mixed and 5 g of 2 % isopropanol solution of chloroplatinic acid was added, and

the reaction was carried out in the same manner as described in the practical example 1. Thus, a silicone gel composition was obtained. The silicone gel compositions prepared in the practical examples 1, 2, and 3 were soft gel and showed a fine extendability on the skin and refreshing feeling after use. At the same time, these gel compositions were stable. In contrast, the gel composition prepared by the method described in the comparative example 1 was hard organopolysiloxane polymer. When the polymer was mixed with a low viscosity silicone oil were mixed, the miscibility was poor and unstable gel composition was obtained.

Cosmetic products containign silicone gel composition prepared by the method described in the present invention are shown in the following.

#### Practical example 4

Foundation ( Composition ingredients )	( Weight Parts )
(1) titanium oxide	14.0
(2) mica	3.0
(3) coloring pigment	3.0
(4) silicone gel composition prepared in the practical example 1	80.0

#### ( Manufacturing method )

The ingredients (1) - (3) were mixed and pulverized uniformly and were added to the ingredient (4). After dispersing uniformly, the dispersion was filled in a container.

#### Comparative example 2

A foundation was prepaerd in the same manner as described in the practical example 4 except that 16 parts of microcrystalline wax and 64 parts of dimethyl polysiloxane ( viscosity 5 cs ) were substituted for the ingredient (4) prepared in the practical example 1.

The sensory test and the storage stability test were carried out on the coundations prepared in the practical example 4 and the comparative example 2. The results are shown in Table 1.

The sensory test was carried out by a panel consisting of 20 female examiners and the evaluation subjects listed in Table 1 were evaluated according to the following standard.

excellent 3 pont

Good 2 points

bad 1 point

◎ : average score is higher than 2.5 points

○ : 1.5 - 2.5 points

X : less than 1.5 points

The storage stability was evaluated as follows; in other words, the test composition was allowed to stand at room temperature for one week and the appearance was evaluated visually.



O : good

X : bad

Table 1:

		a	b
		実例 4	比較例 2
c	さっぱり感	○	○
d	べたつきのなさ	○	×
e	のび	○	×
f	化粧膜の均一性	○	○
g	化粧もち (耐水性)	○	○
h	安定性	○	×

a: practical example 4, b: comparative example 2,  
c: refreshing feeling, d: no greasiness, e: extendability,  
f: uniformity of cosmetic film, g: durability of cosmetic activity  
( water resistance ), h: stability.

As shown in Table 1, it is obvious that the usability and use feeling of the foundation prepared in the practical example 4 were superior to those of the foundation prepared in the comparative example 2. Furthermore, the foundation prepared in the comparative example 2 exhibited a separation of oil ingredient after storing. However, the foundation prepared by the method described in the present invention demonstrated a fine storage stability. In other words, the quality and effective products were obtained without using wax when the present invention was applied.

#### Practical example 5

##### Hand cream

( Composition ingredients )

( Weight parts )

- |  |      |
|--|------|
| (1) silicone gel composition prepared in the practical example 1 | 88.0 |
| (2) octamethyl cyclotetra siloxane                               | 10.0 |
| (3) vaseline   | 2.0  |

( Manufacturing method )

The ingredients (1) - (3) were mixed and kneaded uniformly, and the mixture was filled in a container.

The hand cream prepared by the method described above exhibited a refreshing feeling without greasiness and demonstrated a fine water repelling activity, and at the same time, the storage stability of the product was excellent.

#### Practical example 6

#### Face cream

( Composition ingredients )	(weight parts)
(1) stearic acid	2.5
(2) cetylalcohol	1.7
(3) silicone gel composition *	20.0
(4) sorbitane sesqui oleate	1.0
(5) polyoxyethylene sorbitane monooleate	2.0
(6) triethanolamine	0.7
(7) 1,3-butyleneglycol	5.0
(8) polymetharylic acid	0.5
(9) purified water	balance

\* The silicone gel composition was prepared in the same manner as described in the practical example 1, except that octamethyl cyclotetra siloxane was used as a low viscosity silicone oil.

#### ( Manufacturing method )

The ingredients (1) - (5) were mixed and dissolved by heating at 80° C ( the oil phase ingredient ). The ingredients (6) - (9) were mixed and dissolved by heating at 80° C ( water phase ). The water phase was added gradually into the oil phase ingredient with a constant stirring and an emulsification was carried out. After cooling, the emulsion was filled in a container.

The face cream prepared by the method described above ( Practical example 6 ) demonstrated an excellent extendability on the skin and refreshing feeling without greasiness. Thus, the use feeling and the usability of the said face cream were excellent and at the same time, the storage stability of the composition was excellent.

#### ( Effect of the invention )

As described above, the silicone gel composition prepared by the method described in the present invention demonstrated a fine storage stability, excellent extendability on the skin without inducing greasiness and provided a refreshing feeling, and the use feeling was soft and smooth and the usability was excellent.

The silicone gel composition described in the present invention can provide a product showing a proper viscosity and at the same time demonstrates a structural viscosity, excellent lubrication, water repelling activity and is safe on the skin. Thus, the product has many merits.

Accordingly, when the said silicone gel composition is added to cosmetic compositions, the product can be used as the conventional silicone oil and the cosmetic product exhibiting various merits of silicone oil can be prepared.

Even when a large amount of the silicone oil composition is used in the cosmetic product, no greasiness is noted. Moreover, the cosmetic product exhibits a fine extendability and refreshing feeling in addition to a fine water repelling activity. In addition to the said

merits, the cosmetic product can protect the skin and the hair and provides proper moisture. Therefore, the durability of the make-up cosmetic product may be improved.

When the silicone gel composition is added to the solid or paste oil cosmetic compositions containing wax as the major ingredient, the greasiness is reduced and the separation of oil is prevented. Thus, the storage stability of the cosmetic composition can be improved significantly. Therefore, the silicone gel composition of the present invention can be used effectively in the product containing silicone as the base.

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